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CHEMICAL TECHNOLOGY DIVISION

UNIT OPERATIONS SECTION

MONTHLY PROGRESS REPORT

DECEMBER 1956

OAK RIDGE NATIONAL LABORATORY

OPERATED BY

UNION CARBIDE NUCLEAR COMPANY

A Division of Union Carbide and Carbon Corporation

POST OFFICE BOX X • OAK RIDGE, TENNESSEE

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Report No. CF-56-12-128

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MONTHLY PROGRESS REPORT

December 1956

J. C. Bresee

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MAY 22 1957

OAK RIDGE NATIONAL LABORATORY

Operated by

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P. O. Box X

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Note: The primary objective of this report is the monthly distribution of experimental data as acquired during that period in the course of engineering studies. Much of the data is of preliminary nature and, therefore, reasonable care should be exercised in its application. You are invited to contact the individual authors for substantiation of the data.

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SUMMARY

1.0 EXCER

The dehydration of Excer-produced $UF_4 \cdot 3/4 H_2O$ using a fluidized bed resulted in a water content of the product of 0.05%. During the dehydration the mercury contamination was reduced from 1.7% to 10 ppm but the 0.43% SO_4 concentration was unchanged during the 4 hr of dehydration in nitrogen at 410-510°C.

2.0 FLUOROX

The reaction velocity constant for the reaction $UF_4 + O_2 \longrightarrow UF_6 + UO_2F_2$ was expressed by the equation $\ln k = 13.3 - 14.9 (1000/T)$.

3.0 HR FUEL AND BLANKET PROCESSING

High Pressure Flange Closures - Cold physical tests of Belleville springs to be used on HRT-CP flange bolts has been completed. Yield points and spring deflection data are reported for the springs on hand.

Hydroclone Development Studies - A 0.56-in. dia hydroclone having a predicted capacity of 1.28 gpm is being fabricated for test purposes.

Synthetic Solids Production - A total of 3 kg of synthetic fission and corrosion products solids were produced for HRT-CP and dissolver studies.

P-1 Loop - The P-1 loop has been prepared for water operation after replacing the main loop pump head gasket. The hollow stainless steel oval ring gasket supplied with the pump did not seal properly.

P-2 Loop Component Tests - The all titanium pump for loop P-2 was tested and found to perform as predicted from design curves. Heads of 52 ft at 60 cycle/sec and 109 ft for 95 cycle/sec power were measured.

P-2 Loop Sampler - A sampler for the in-pile loops was tested on loop P-2 operating at 300°C. The sample volumes ranged from 11 to 13 ml, within design criteria.

4.0 ION EXCHANGE

In the 36-in. resin test loop 130 ft³ of resin (Permutit SK, 10-20 mesh) was pulsed using a hydraulic accumulator with a minimum of 20 psi pressure drop across the contactor. The 12-in. contactor at Grand Junction operated at a minimum pressure drop of 40 psi.

Testing of a Pu-U isolation system in a 3-in. dia column using iron in place of plutonium has begun. Drawings are nearly complete for a 200 ton/day ore contactor and a scrap recovery installation for the Y-12 plant.

5.0 METALLEX

Revisions are being made in transfer piping and in the ThCl₄ salt feed system to facilitate operation and to improve product purity, in the large-scale contactor.

6.0 POWER REACTOR FUEL REPROCESSING

Zircex - The hydrochlorination rates of cold worked U-Zr alloys did not appear to be markedly different from those obtained for cast U-Zr alloys. Data scatter prevents a quantitative comparison at this time. The hydrochlorination of 60% U-40% Zr alloy at 600°C gave a uranium loss of 1.2-2.0% as insolubles when the resulting UCl₃ was dissolved in 8 M HNO₃. Uranium transfer to the vapor phases by volatilization and entrainment³ was 0.02%.

Darex - A bench scale continuous dissolver for the dissolution of U-stainless steel alloys (and sinters) has been constructed and a shakedown run made.

HCL Distillation - A 4-in. dia 12 plate glass column containing 1 bubble cap per plate reduced the chloride concentration in a simulated Darex dissolver solution from 1.7 N Cl⁻ to less than 20 ppm. The desired level is ~35 ppm.

Mechanical Processing -

Decladding Studies - Coextruded zircaloy-2 cladding was successfully removed from 3 ft long 0.3-in. dia natural U rod, in 5 passes through the Mackintosh-Hemphill Rotary Straightener. Indented or scored stainless steel cladding split along the indentation or scoring when subjected to the pressure of a Mackintosh-Hemphill Rotary Straightener.

Disassembly Studies -

(Elox Electrical Discharge Cutting)

A 0.020-in. dia brass wire electrode cut stainless steel at the rate of 0.021 in.³/hr (rated cutting capacity, 0.036-in.³/hr).

Wire cutting appears feasible only for very difficult cutting operations in which conventional means cannot be used.

Saw

A saw capable of separating core and blanket segments of a single fuel element and removing end boxes by transverse cutting has been designed.

Discharging Dissolver Solids - A novel, critically safe, continuous dissolver has been designed. Demonstration runs with sheared pieces of stainless clad natural U cores are planned.

Pulse Column Interfacial Solids Removal - A fine Fulflo glass fiber will remove the solids from a solvent extraction column interface but it will not always break the emulsions accompanying the solids.

Materials Evaluation

Corrosion Studies - Titanium suffered negligible corrosion in simulated Zircex solutions. Battelle Memorial Institute will perform the corrosion work previously done by UNOP.

Radiation Damage Studies - Radiation damage studies of paints and plastics in the HRT will be delayed for an indefinite period.

Specimens of Haveg 093 have been ordered for radiation damage studies. This carbon filled plastic may be useful as a material of construction in reprocessing U-Zr alloy fuels.

7.0 SUBCONTRACTS

Development of thermal diffusion column theory is progressing with attention centered on simplifying assumptions to avoid the necessity of attacking the non-linear differential equations resulting from rigorous considerations. Equipment is under construction to measure the Soret coefficient and the thermal diffusion coefficient for metallic ion separation.

8.0 VOLATILITY

The KOH spray tower for fluorine disposal has a capacity of at least 2.7 scfm of pure fluorine. Gas-liquid contacting studies have shown a dip tube to be more efficient as a contacting device at high gas rates (5.0 cfm) and a baffled draft tube to be more efficient at low gas rates (0.25 cfm). Data are presented showing the effect on gas utilization efficiency of gas flow rate, dip tube depth, and location, draft tube diameter, diameter of gas inlet to draft tube, vessel diameter, and liquid and gas concentrations.

1.0 EXCER

C. W. Hancher, R. O. Payne

The purpose of the Excer Program is to develop a low temperature, aqueous chemistry method for producing UF_4 . The Excer process consists of four sections: (1) feed preparation, (2) reduction and precipitation, (3) filtration and drying, and (4) dehydration. During the past 30-day period dehydration has been the only section of the Excer process studied.

Dehydration

A batch 3-in. dia fluidized bed was tested for dehydration of Excer UF_4 hydrate (Fig. 1.1). The UF_4 hydrate had been produced from a falling film mercury cathode Excer cell using H_2SO_4 as the current carrying electrolyte. The material had been dehydrated to 0.64% H_2O using the Excer screw dehydrator, and was sized to -30, + 100 mesh.

The UF_4 hydrate was added to the cold fluidized bed, heated and fluidized for 3 hr before the bed was at $400^\circ C$. After 2 hr at $400^\circ C$, the water content was reduced to 0.05% (Table 1.1). This is an acceptable water concentration for further processing. The mercury contamination was reduced from 1.7% to 10 ppm after 7 hr; however, the SO_4^{2-} concentration was not reduced during dehydration.

Figure 1.1

EXPERIMENTAL FLUIDIZED BED OXIDATION REACTOR

TABLE 1.1

Fluidized Bed Dehydration of Excer Product $UF_4 \cdot 3/4 H_2O$

Temperature 410-510°C Bed Diameter 3 inches Bed Depth 10 inches N ₂ Gas Flow 40 cfh Bed Pressure Drop 6 inch Hg Size of UF ₄ -30 +100 mesh				
Time After Start-Up (hr)	U ⁺⁴ (%)	H ₂ O (%)	Hg (ppm)	SO ₄ (%)
0	67.81	0.64	17,000	0.42
3	67.76	0.16	8,200	0.43
4	67.53	0.05	100	0.45
5	67.66	0.05	37	0.45
6	67.53	0.05	10	0.45

3 hours required to reach 400°C

2.0 FLUOROX

J. B. Adams, J. Cowles,¹ G. Jensen,¹ D. H. Newman

Results of 2 additional fluidized bed oxidation runs are presented. The variation of reaction velocity constants with temperature of all 5 runs completed was estimated as $\ln k = 13.3 - 14.9 (1000/T)$ within approximately a factor of 2. The equation permits extrapolation of reaction rates at temperatures above the experimental range.

2.1 Oxidation

Two additional UF_4 oxidation runs were completed. Runs were of 60 and 10 hr duration at temperatures of 650 and 717°C. Kinetic data from all 5 runs to date have been correlated by a single equation.

2.1.1 Oxidation Runs

Data for Runs 4 and 5 are presented in Tables 2.1 and 2.2. The temperature in Run 4 was 650°C for about the first 30 hr but dropped after this time because of the low level of solids in the reactor. From 30 to 60 hr the temperature was believed to be close to 560°C. Only data from the first 30 hr of operation were used for calculations. Included with the regular sample analysis are 3 samples of scale scraped from the wall of the reactor at various times. The temperature in Run 5 ranged from 600 to 717°C. The run was started at 600°C, raised to 717°C over a period of 3 hr, then maintained at about 717°C for 9 hr. In both runs, gas flow rates of 35 to 38 CFH (70°C, 1 atm) of oxygen were used to fluidize 3000 g/ UF_4 charges. Details of operating techniques are given elsewhere.²

2.1.2 Kinetics

Data from Runs 4 and 5 were treated as were previous data² using a plot of $y/(1 - 0.51 y)$ vs. time on a semi-log to determine k , the reaction velocity constant, in the equation $-d(w)/dt = k(w)$, which is assumed to apply for this reaction. The symbol y represents the weight fraction and w the weight of UF_4 present in the reactor at any time.

¹ M. I. T. Practice School

² Unit Operations Monthly Report November 1956 (CF#-56-11-143).

TABLE 2.1

Fluidized Bed Oxidation of UF_4
Chemical Analyses for Run 4⁽¹⁾

No.	Condition	Elapsed Time-Hrs.	%U _{TOT}	%U ⁺⁴	%WSU ⁽²⁾	%F	%AOI ⁽³⁾	%Ni	%C	%H ₂ O
1	(Scale sample)	---	49.22	---	---	13.77	---	5.43	---	---
2	N ₂ Flow	0	75.76	68.09	9.07	21.1	7.00	---	.01	0.68
3	N ₂ Flow	0	---	---	---	21.32	---	---	---	0.21
4	N ₂ Flow	0	---	---	---	21.64	---	---	---	---
5	N ₂ Flow	0	74.60	69.51	9.70	21.59	6.79	---	---	---
6	N ₂ +O ₂ Flow	0	75.87	68.11	---	21.3	7.05	---	.01	---
7	O ₂ Flow	0.80	74.44	58.60	15.8	21.5	1.62	---	---	---
8	O ₂ Flow	2.80	74.44	55.41	---	21.3	---	---	---	---
9	O ₂ Flow	4.97	75.68	54.86	---	20.8	---	---	---	---
10	O ₂ Flow	5.80	74.60	48.93	30.0	19.9	0.30	0.12	<.01	---
11	O ₂ Flow	8.80	75.28	47.01	---	19.5	---	---	---	---
12	O ₂ Flow	11.05	75.50	45.18	---	20.0	---	---	---	---
13	O ₂ Flow	12.72	75.59	43.19	---	19.2	---	---	---	---
14	O ₂ Flow	15.32	74.80	42.74	35.9	18.6	0.64	---	---	---
15	O ₂ Flow	18.32	74.86	42.92	---	18.2	---	---	---	---
16	(Scale sample)	---	73.96	47.31	---	19.6	---	1.58	---	---
17	O ₂ Flow	21.32	74.75	35.29	---	18.0	---	---	---	---
18	O ₂ Flow	25.23	71.67	34.23	---	16.7	---	---	---	---
19	O ₂ Flow	29.23	74.06	26.56	---	17.2	---	---	---	---
20	O ₂ Flow	33.23	74.14	29.98	45.5	16.5	1.16	.06	<.01	---
21	O ₂ Flow	37.23	74.45	28.04	---	16.6	---	---	---	---
22	O ₂ Flow	42.53	74.78	28.83	---	16.6	---	---	---	---
23	O ₂ Flow	46.55	74.66	29.11	---	16.8	---	---	---	---
24	(Scale sample)	---	74.44	27.83	---	16.3	---	---	---	---
25	O ₂ Flow	50.20	74.68	25.89	---	16.6	---	---	---	---
26	O ₂ Flow	56.03	74.58	25.60	---	16.7	---	---	---	---
27	O ₂ Flow	59.53	74.22	26.33	48.4	16.4	2.91	---	---	---

(1) About 35 SCFH O₂ through a 3000g batch charge at 650°C for about 30 hrs., lower temperatures for second 30 hrs.

(2) % water soluble uranium

(3) % ammonium oxalate insoluble

TABLE 2.2

Fluidized Bed Oxidation of UF_4
Chemical Analysis for Run 5⁽¹⁾

No.	Condition	Elapsed Time-Hrs.	% U_{TOT}	% U^{+4}	% W.S.U. ⁽²⁾	% F	% AOI ⁽³⁾
1	N_2 Flow	0	75.54	65.05	12.1	20.7	8.82
2	$O_2 + N_2$ Flow	4.35	73.38	53.93	25.4	19.9	1.07
3	O_2 Flow	5.00	75.42	49.04	---	19.6	---
4	O_2 Flow	5.93	76.08	45.94	34.3	18.1	0.40
5	O_2 Flow	6.43	75.74	41.14	---	18.4	---
6	O_2 Flow	7.27	75.36	40.67	---	18.4	0.15
7	O_2 Flow	8.37	74.82	37.51	40.7	17.8	0.26
8	O_2 Flow	9.43	76.49	32.60	---	16.8	---
9	O_2 Flow	10.42	76.14	24.52	---	16.2	---
10	O_2 Flow	11.50	75.20	23.64	(59.8)	15.6	0.34

(1) About 35 SCFH O_2 through a 3000g batch charge at $717^\circ C$ for about 9 hrs.
 Oxygen flow was started at $600^\circ C$ and temperature reached $717^\circ C$ after 3.0 hrs.

(2) % water soluble uranium

(3) % ammonium oxalate insoluble

Plots for the determination of k are shown in Fig. 2.1. Data for Run 4 are scattered, as are the analytical data for that run. Data for Run 5 are fairly consistent, however. Values of k were determined as 0.034/hr at 650°C and 0.162/hr at 717°C. Figure 2.2 shows a plot of k vs. $1/T$ for all 5 runs to date. A straight line fitted to the data gives the equation $\ln k = 13.3 - 14.9 (1000/T)$.

2.1.3 Proposed Work

Future plans for fluidized bed UF_4 oxidation studies include:

1. The study of carbon monoxide combustion in the fluidized bed for internal heating to supplement or replace external heating through the walls.
2. Further oxidation runs to confirm and extend present reaction rate data as a function of temperature and possibly of oxygen partial pressure (by the use of air).
3. The study of corrosion of Inconel and possibly a few other alloys during these experimental runs.
4. Design, construction and operation of a continuous fluidized bed UF_4 oxidation system when sufficient data are accumulated.

Equipment modifications being prepared are a new off-gas system for handling UF_6 and design of a flame reactor to react UF_4 and oxygen in a carbon monoxide-oxygen flame.

Figure 2.1

Plot for Determination Reaction
Velocity Constant

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Figure 2.2

Variation of Reaction Velocity
Constant with Temperature

3.0 HR FUEL AND BLANKET REPROCESSING

E. O. Nurmi

Engineering evaluation and equipment development studies were continued on high pressure flanges, hydroclones, corrosion product solids, loop P-1 and loop P-2 components. Results of these studies for the past month are reported.

3.1 HRT-CP Test of Sampling Device for In-Pile Loops

R. W. Horton, R. D. Arthur, J. Beams, V. L. Fowler, F. N. McLain, D. A. McWhirter, G. E. Woodall

A preliminary model of a sampler of possible value for in-pile loops has been constructed from a design originated by the Chemical Technology Design Section. This unit was operated successfully on B-2 loop. Sample volumes removed ranged from 11 to 13 ml and sampler cooling held all temperatures below 100°C during 1 hr circulation periods. The differential piston was powered with nitrogen gas with satisfactory results.

The sampler design is shown in Fig. 3.1. A thermocouple well (not shown) was drilled in the sampler body to a point about 0.25 in. from the small diameter "O" ring. The unit was connected to B-2 loop, using 0.083 in. i.d. tubing rather than the capillary tubing which would be used in sampling an in-pile loop. The larger tubing results in a greater circulation rate through the sampling chamber and consequently a greater cooling load than was contemplated in the original design. With the incoming sample stream at ~300°C and ordinary process water circulated through the cooling jacket, the maximum temperature recorded by the thermocouple adjacent to the "O" ring was 25°C. This temperature was maintained for sample circulation periods of 1 hr, thus demonstrating that the cooling system is adequate to protect the "O" ring seals.

The loop was operated at 300°C and 2000 psi with demineralized water. The feed was water to which 2.0 g/liter of ZrO_2 had been added. Samples were taken hourly from the test sampler and the conventional loop sampler, and the sample volume was replaced with the ZrO_2 suspension feed. The samples were not analyzed, but showed no visual difference in solids concentration in samples from the two different points. Table 3.1 shows volumes removed through the sampling unit. Two consecutive samples were taken every hour. A separate series of tests was run to determine the reliability of feed was run to determine the reliability of feed injection through the sampler, using nitrogen pressure on the differential pressure to force feed into the loop against pressure. These results are shown in Table 3.2

The design feature in this sampler unit which is most questionable is the use of "O" ring seals. These seals did not leak in the test series, but since they would be exposed to radioactive materials if used for in-pile loop sampling their reliability would be questionable. This feature has been recognized by the design group and will be corrected if further work is done on this type of sampler.

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SECTIONAL VIEW OF PRESSURE GENERATOR

Figure 3.1

TABLE 3.1

Record of Sample Volumes Removed from Loop with
Differential Piston Sampler

<u>Conditions:</u>			
Loop Temperature 300°C			
Loop Pressure 2000 psi			
Loop Solution ZrO ₂ suspension in H ₂ O (~250 mg/kg)			
Sampling Frequency 2 consecutive samples/hr (except last 3 hr)			
	Time	Volumes of 2 Samples	
11-20	1900	11.0	11.0
	2000	12.0	11.0
	2100	12.0	13.0
	2200	12.0	12.0
	2300	12.0	12.0
11-21	0005	11.5	12.5
	0100	12.5	12.0
	0200	12.0	12.0
	0300	12.0	12.0
	0400	12.0	12.0
	0500	12.0	12.0
	0600	12.0	12.0
	0700	12.0	12.0
	0800	12.5	12.5
	0900	12.0	12.0
	1000	12.0	12.0
	1100	12.0	12.5
	1120	12.5	12.6
	1140	12.0	12.6
	1200	13.0	13.0
	1220	12.4	12.2
	1240	12.8	12.8
	1300	12.6	13.0
	1320	12.8	12.4
	1340	13.0	12.0
Average of all samples 12.2			

TABLE 3.2

Test of Feed Injection Through Differential Piston Sampler

<p><u>Conditions:</u></p> <p>Loop Temperature 75°C</p> <p>Loop Pressure 1800 psi</p> <p>Feed - Demineralized H₂O</p> <p>N₂ at 800 psi used for power source</p>	
<u>Test No.</u>	<u>Volume Injected</u>
1	10.4
2	10.0
3	10.0
4	9.6
5	10.2
6	10.6
7	10.0
	Average 10.1

3.2 High Pressure Flange Tests

C. C. Haws, Jr., J. Beams, R. C. Early, F. N. McLain

Cold physical testing of the belleville springs proposed for use on the CPP flanged joints has been completed. A single run in which these springs have been tested on flanges under simulated CPP operating conditions has also been completed. Data collected in these efforts are inconclusive and do not show at present any marked advantage in the use of these springs. Further work will be done to check the data already collected and to find where any fault might lie.

Table 3.3 gives a tabular description of the belleville springs and pertinent data obtained in cold physical testing.

Examining Table 3.3 and recalling that hot bolt loadings have exceeded 20,000 lb on occasion, it was decided to test first a system of three springs in parallel. Further, since a bolt loading of 6000-7000 lb is required to obtain a tight seal, bolt loadings of 7000-8000; 8000-9000; and 9000-10,000 lb were selected for assemblies 1, 3, and 4 (Table 3.4). Thus after relaxation of both the joint and the springs, sufficient bolt load should remain within the range selected to assure a leak tight joint in one of the cases. Assembly 2 used the cadmium plated bolts now in service in the CPP and was included in the test loop as a reference.

The data of Table 3.4 indicate the following:

1. A relaxation amounting to some 1000 lb (expressed bolt loading) occurs at room temperature within a few days following flange assembly. (Compare columns headed 10/23 and 10/29.) Following the readings taken on 10/29, no further change in bolt loading occurred. These latter data are not shown.
2. After initial relaxation (or creep), the bolt loading of the joint levels off and no detectable further creep occurs through the thermal cycling.
3. Creep, as indicated by lengthening of the bolts, was not detectable. The change in length of the bolts is shown in the table, with the average change being a loss of length equal to 0.00029 in. This loss undoubtedly occurred through repeated cleanings and the slight oxidation of the measuring surfaces.
4. Specification given the manufacturer of the belleville springs required a 0.003 in. deflection upon increasing the bolt loading from 3000 to 3850 lb. The physical data of Table 3.3 and the hot loading data from Table 3.4 show that this specification was not fulfilled. A comparative improvement is noted where the springs are used, but not enough to justify their use. Further tests will be conducted on series-parallel arrangements

TABLE 3.3

Descriptive and Physical Test Data for Belleville Springs

Descriptive Data	(in.)
Outside diameter	1-3/4
Inside diameter	0.765
Thickness of metal	0.156
Approximate dish height at rest	0.040
Deflection of a single spring	
at 3000 lb.	0.0077
at 4000 lb.	0.0094
Physical Data	(lb.)
Apparent Yield Points	
Single spring	5,000
Two springs in parallel	11,000
Three springs in parallel	18,000

Material - Inconel X

TABLE 3.4

High Pressure Flange Studies

Bolt Loadings Using Belleville Springs
Run No. 6 14 Thermal Cycles

Assembly No.	Bolt No.	Bolt Load on Assembly 10/23 to 10/26 (lb)	Bolt Loading ¹ Cold on 10/29 (lb)	Hot Bolt ² Loading on 11/2 (lb)	Bolt Load Cold on 12/3 (lb)	Hot Bolt ³ Loading on 12/7	Bolt Loading Cold at End of Run 12/10	Change in Bolt Length (in. x 10 ⁻⁴)
1 Belleville Springs	S1	7,600	5,200	15,100	5,700	15,400	3,800	+ 3.5
	S2	7,600	6,800				8,600	-11.5
	S3	7,900	6,000				9,200	- 5.5
	S4	7,000	5,200	14,000	4,300	14,300	4,800	+ 5.5
	Avg.	7,530	5,800				6,600	
2 CPP Bolts only	B1	-	-	-	-	-	6,500	- 1.5
	B4	7,000	6,500	-	-	-	6,200	- 3.5
	B5	6,100	4,800	20,000	6,200	20,800	4,500	- 3.5
	B6	6,100	4,800	20,000	5,300	21,700	5,200	- 5.5
	Avg.	6,400	5,400				5,600	
3 Belleville Springs	S5	8,700	8,100				7,600	- 4.5
	S6	9,200	7,800				8,100	- 5.5
	S7	8,900	8,700	17,600	8,700	19,000	8,800	- 5.5
	S8	8,900	8,700	17,300	8,400	19,000	7,800	- 3.5
	Avg.	8,900	8,300				8,100	
4 Belleville Springs	X1	10,900	8,700	16,800	8,200	17,300	8,900	- 0.5
	X2	10,900	8,900				8,600	+ 4.5
	X3	11,100	10,600				10,600	- 4.5
	X4	10,900	9,200	18,100	10,800	19,200	10,300	- 4.5

¹ Before thermal cycling² Cycle 11³ Cycle 14

of these springs and on a system using two springs in parallel.

Table 3.5 gives the data of interest regarding temperatures and times of the thermal cycles. The thermal shock as given by heat-up and cool-down times is the same as encountered in previous runs. No leaks were found during the run.

3.3 HRT-Hydroclone Development Studies

P. A. Haas, D. A. McWhirter, V. L. Fowler

0-56 in. dia. Hydroclone - A 0.56 in. dia. hydroclone has been designed and is being fabricated as possible replacement for the HRT-CPP hydroclone. This unit will fit the present flange and has a predicted capacity of 1.28 gpm at 100 ft compared to 0.73 gpm for the present unit. The predicted B/F rate for this new unit (length = 3.20 in.) is 2.0%.

3.4 HRT-CP Synthetic Solids Production and Dissolution

P. A. Haas, N. A. Brown

A total of about 3 kg of synthetic fission and corrosion product "mud" was produced. About 2 kg have been used for HRT-CPP solids deposition studies; the other kg is to be used for dissolution studies in a tantalum-lined pot. When the initial batches of product showed high halide concentrations, an NH_4OH wash procedure was used for several batches. The NH_4OH washed product showed lower halide concentrations, but succeeding batches made without the NH_4OH washes showed still lower amounts of halides. Whether these results are due to analytical inaccuracies or due to feed or procedure changes is not known.

Installation of a tantalum-lined dissolver and associated equipment is about 95% complete. This system is a mockup of the HRT-CPP system and will test out the procedure for dissolution with H_2SO_4 .

3.5 HRT-Blanket Processing Loop P-1

S. D. Clinton, P. A. Haas, G. E. Woodall

Loop P-1 will be operated with water for a period prior to the UO_2SO_4 blanket processing studies, this period of testing with water is expected to start during the week of December 17. Testing and minor alterations of accessory systems including the waste, vacuum, and cooling water systems has been completed. Based on REED and HRT-CPP experience, the hollow stainless steel oval ring gaskets in the head end of the A-150 pump have been replaced. A teflon gasket has been used under the thermal barrier and a solid 0.081 in.-dia. gold ring for the scroll case. Installation of the initial loop design including the thermoprobe and other instrumentation was completed the week of December 7.

TABLE 3.5

High Pressure Flange Studies

Thermal Cycle Data from Belleville Spring Test

Run No. 6

Cycle No.	Time to Heat to 290°C (hr)	Time above 290°C (hr)	Equilibrium Temperature (°C)	Time Cooling to 100°C (hr)	Time Cooling to 75°C (hr)	Minimum Temperature Reached (°C)
1	1.2	1.4	290	2.5	3.3	40
2	1.2	10.8	288	2.7	3.3	57
3	1.5	1.0	288	6.9	7.5	78
4	1.6	1.1	291	2.7	3.8	35
5	1.85	3.8	308	3.1	4.0	81
6	0.65	2.1	306	3.9	4.9	34
7	0.90	1.7	311	4.2	5.2	85
8	1.66	1.7	242	2.2	3.2	50
9	5.5	-	286	4.5	6.2	67
10	7.5	1.2	298	3.5	4.7	-
11	1.5	6.4	300	4.1	5.6	65
12	.6	1.5	298	3.3	4.3	63
13	.8	1.7	298	3.1	4.2	42
14	~1.0	109.2	307	-	-	-

Total time above 290°C $\approx$ 142 hrs.

3.6 HRT-Blanket Processing Loop P-2 Component Studies

P. A. Haas, V. L. Fowler, D. A. McWhirter, G. E. Woodall

3.6.1 Heat Exchanger - A prototype of a proposed loop P-2 heat exchanger has been received and set up for testing. This unit, which uses three parallel stainless steel water tubes and three parallel titanium blanket solution tubes all cast in aluminum, will be tested with process water and 100 psia steam.

3.6.2 Titanium Pump - The all titanium pump of a modified ORNL design for loop P-2 has performed as expected during tests with water at room temperature. This design (as shown by drawing D-27001) has two aluminum oxide bearings and a 4 in.-dia. impeller. The observed output heads (Fig. 3.2) agreed with the 52 ft at 60 cycles/sec and 109 ft for 95 cycles/sec predicted by an empirical equation for the ORNL pump design (ORNL-2057, p. 49).

$$H = 0.0122 D^{1.3} f^{1.6}$$

D = impeller dia. in inches

f = electrical supply frequency, cycles/sec.

H = pump output head in ft of liquid for 0-2 gpm.

Four 1/8 in.-dia. holes were drilled in the impeller to reduce the bearing thrusts to less than 10 lb for all possible operating conditions. The initial thrust at 5 gpm, 60 cycles/sec. was 20 lb toward the head end of the pump.

FIGURE OUTPUT OF LOOP P-2 PUMP

4.0 ION EXCHANGE

C. W. Hancher, J. S. Taylor

The Ion Exchange Program was initiated to develop ion exchange equipment and processing steps for existing and new flowsheets. The problems now under consideration in the ion exchange program are: (1) the 36-in. resin test loop (2) the Y-12 uranium scrap recovery problem (3) the plutonium-uranium isolation contactor test (4) the design and cost estimation for 200-400 ton/day Higgins type ore contactor and (5) the sub-contract work being performed by the University of Tennessee, Chemical Engineering Department, using a hydraulic ram contactor.

4.1 36-Inch Resin Test Loop

Water distribution and resin movement data are being obtained on the 36-in. resin test loop by a study group from the M.I.T. Practice School. The minimum pressure drop to move the resin was found to be 20 psi.

4.2 Y-12 Uranium Scrap Recovery

The fabrication and installation drawings for the Y-12 scrap recovery problem job are 80% completed.

4.3 3-Inch Pu-U Isolation Contactor

The M.I.T. Practice School is operating the 3-in. dia. Pu-U isolation contactor with a Fe-U system to determine stage heights, equilibrium time, and general hydraulic operating conditions.

4.4 200 Ton/Day Contactor

The design and fabrication detail drawings for a large scale contactor (200-400 ton/day) is 90% complete.

4.5 University of Tennessee-Ion Exchange Sub-Contract

The University of Tennessee, Chemical Engineering Department, sub-contract for ion exchange studies has been applied to the development of a 4-in. dia. hydraulic ram ion exchange contactor. A water softening study has been undertaken to investigate the contactor operating efficiency. In addition, a basic differential transfer investigation in packed ion exchange beds is being carried out.

5.0 METALLEX

G. K. Ellis

J. C. Rose, R. O. Payne, and W. G. Sisson

The revisions considered necessary to insure continuous removal of reacted contents of the 1.5 gal Dispersall contactor have been completed (Fig. 5.1 and Fig. 5.2). The current revisions to facilitate operation of the process and increase product purity by carrying out all operations prior to the wash stage in an inert dry atmosphere are about 50% complete and will include the following items, the first two of which are complete and installed.

- (1) Provisions for placing a vacuum of 24 in. of Hg on either of the coagulation tanks.
- (2) A dry box adaptation for feeding ThCl_4 salt from 40 gal barrels, in an inert dry atmosphere, to the contactor (Fig. 5.3).
- (3) Sparging of coagulation tanks with helium.
- (4) Installation of a transfer system to accomplish either rewashing or refiltration of product, transfer of filtrate to product transfer tank, and transfer of amalgam to the amalgam feed tank on top floor level.
- (5) A heat exchanger in the amalgam feed line for secondary control of the amalgam temperature.
- (6) A condenser for the 15 psig steam to furnish pure water for the wash column.

A 2-hr run has been made using amalgam only as the feed material. Appearances are that the problem of continuous removal of reactor contents has been solved. A further extended run will begin immediately, a temporary delay having occurred in replacement of a defective pump in the contactor cooling line. A complete run will be simulated, carrying the amalgam through the contactor, wash column, coagulation tanks, filtration step, and transfer from the process location to the metallurgy press location. The mercury will then be transferred to the product pressurizer tank and forced into the die and punch assembly of the press by helium pressure. The purpose of this routine will be to locate as many operational problems as possible before introducing thorium tetrachloride in the process.

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Fig. 5.1 Metallex 1.5 Gal Dispersall Connector

Photo-19257
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Fig. 5.2 Metallex Wash Column

Fig. 5.3 Metallex Salt Feed Dry Box

6.0 POWER REACTOR FUEL REPROCESSING

C. D. Watson

Problems active during this period were:

- 1) Zircex
- 2) Darex
- 3) HCl Distillation
- 4) Mechanical Processing
 - Disassembly Studies
 - Decladding Studies
- 5) Discharging Dissolver Solids
- 6) Pulse Column Interfacial Crud Removal
- 7) Materials Evaluation
 - Corrosion Studies
 - Radiation Damage Studies

Problems inactive were:

- 1) Waste Studies
- 2) Shearing Studies
- 3) Recovery of Spent Solvent with a Hydroclone
- 4) Head End Clarification

6.1 Zircex

J. J. Perona, R. J. McNamee, G. B. Dinsmore

The objectives of the problem are to obtain data for the design of full-scale hydrochlorinators, and to demonstrate the hydrochlorination of zirconium-uranium fuel elements. Examples of power reactor fuels which may be processed eventually by the hydrochlorination reaction are those of the Consolidated Edison, Commonwealth Edison, and Rural Cooperative Reactors.

Studies of the heat transfer aspects of the hydrochlorination process and of reaction rates from 400 to 700°C have been presented in previous reports (October UNOP Monthly CF#-56-10-83 and November UNOP Monthly Report CF#-56-11-143). Studies are continuing on: (1) the effect of metallurgical properties on reaction rate and (2) UCl_3 losses by entrainment and vaporization and (3) dissolution of UCl_3 residue in HNO_3 .

Five runs have been made with extruded U-Zr alloy rod, but the data are too scattered to permit a conclusion to be drawn concerning the effect of cold working on reaction rate. The dissolution of uranium chloride residue in nitric acid was found to leave some insoluble fines which contained about 2% uranium indicating the need for further digestion studies. Losses of uranium by vaporization and entrainment were evaluated for one run and found to be less than 0.02%.

Three runs were made with extruded rod of 30% uranium in the temperature range of 475 to 675°C, and two runs were made with 60% uranium in the range of 425 to 554°C. These data are plotted in Fig. 6.1, along with data for arc-melted rods previously reported. The data are too scattered to permit a conclusion to be drawn concerning the effect of cold working on reaction rate. The amount of cold-working undergone by the extruded rods is not known, but the amount on each rod was the same.

Uranium chloride residue from a run with 60% uranium alloy at 600°C was used in a dissolution study. One part of the residue was boiled in 8 M HNO_3 for one hour and centrifuged, yielding insoluble fines which contained 2.5% uranium. A second portion of the residue was boiled in 8 M HNO_3 for 24 hr, yielding a residue containing 1.5% uranium. The corresponding uranium losses were 2.0% and 1.2%, respectively. These data indicate that uranium might be recovered from insoluble fines by the use of longer digestion times.

6.2 Darex

J. J. Perona, R. J. McNamee, K. J. Fritz, and G. B. Dinsmore

The objectives of this problem are to develop the dissolution process for stainless steel uranium fuels in dilute aqua regia and to demonstrate the continuous dissolution of full scale power reactor fuel elements. Examples of power reactor fuels which may be processed eventually by Darex are those of the Consumers Public Power, Yankee Atomic Power, and Army Package Power Reactors.

Studies to obtain design data include: (1) continuous dissolution rates as a function of acid feed composition and rate (2) effect of metallurgical properties on dissolution rate (3) effect of liquid level in the dissolver on condenser duty (4) off-gas composition and rate (5) condensate composition and rate (6) product stream digestion and clarification and (7) corrosion of construction materials.

Figure 6.1 Effect of Cold-Working on Hydrochlorination Rate

A continuous bench scale dissolver system has been erected to feed the stripping column for HCl removal experiments as well as to produce dissolution data. A shakedown run was made, followed by minor equipment modifications. Runs to obtain dissolution data are now being made. A photograph of the dissolver system is presented in Fig. 6.2.

6.3 HCl Distillation

F. G. Kitts

The purpose of the initial HCl distillation work has been to demonstrate the removal of the chloride ion from the stream leaving the Darex dissolver. The chloride concentration must be reduced to less than 30 ppm to prevent interference with solvent extraction processing and to prevent corrosion of the stainless steel processing equipment. Continuing investigation will include studies of composition of stripping vapor, V/L ratio and metal ion concentration, plate efficiency, and decomposition and off-gas composition.

Analytical results for the run described in last month's report have been received. The feed contained 1.75 M Cl^- , 4.5 M NO_3^- , 3.9 M H^+ and 64 g/liter total metals; the actual V/L for the run was approximately 5. The Cl^- concentrations on the various plates down the column are shown in Fig. 6.3. Samples were taken approximately 1/2, 1-1/2, and 2-1/4 hr after feed was admitted to the top plate of the acid-filled column. This run must be regarded as exploratory, with its main significance being the proof that the chloride ion can be removed from Darex dissolver solution containing dissolved stainless steel and uranium.

Since this run was made, the column has been moved into Cell IB, Building 4505. After reassembly the column was insulated to minimize heat losses. This changed the operating characteristics of the column considerably and added the disadvantage that column functioning can no longer be visually observed. A second run has been made, but some operating difficulties were encountered due to the inability to profit by experience gained in the first run. This run used the same feed as Run #1 but was made with 70% nitric acid by weight as strip and $\text{V/L} = 1$. In this run some acid decomposition (evidenced by NO_2 in the off-gas) was observed that had not been present in Run #1. Analytical results for the run have not yet been received. Other runs will be made in the immediate future to standardize operating conditions and determine maximum throughput.

6.4 Mechanical Processing - F. G. Kitts, G. A. West

6.4.1 Decladding Studies

The purpose of clad removal is to decrease the amount of diluent material accompanying active material through chemical reprocessing, and to allow the use of nitric acid chemistry by removing insoluble clads, exposing

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CONTINUOUS BENCH-SCALE DISSOLVER

Figure 6.3 Chloride Concentration Profile for Darex Distillation.

nitric acid soluble core materials for dissolution. The present program deals with the removal of zirconium and stainless steel clads from various types of core materials. Zirconium clad was removed from a uranium rod and a stainless steel spacing wire was removed from a stainless steel clad.

When long rod-type elements are used in power reactor fuel assemblies, a wire is usually wrapped around the rod in a spiral in order to maintain proper spacing of the rods and to provide coolant channels through the bundle.

To simulate such elements, 36-in. lengths of 9/16-in. dia steel rod were placed inside .035-in. wall thickness S.S. tube with an inside diameter such that there was .012-in. diametral clearance between rod and tube. Around the outside of the tube was wrapped 1/32-in. S.S. wire on a 12-in. pitch. The wire was attached to the tube at the ends and at points 9-in. along the tube by spots of silver solder. Silver solder was used in preference to heliarc welds in order to minimize damage to the rollers of the Mackintosh-Hemphill machine in these preliminary tests.

Rolling began with very light work; the severity of the work as then increased with each pass. Upon rolling, the wire flattened on the exposed side while remaining circular and indenting the clad on the side next to the tube. After several passes the tube had been deeply scarred and indented by the wire, which elongated and did not lie in the same position for each pass. Further rolling failed to expand the tube in the usual manner; instead it tended to rupture at points of deepest penetration by the wire.

Zirconium cladding of .030 wall thickness was removed from two approximately 36-in. long uranium rods 1/4-in. in diameter in five passes through the derodder. The zirconium tubes expanded only about 0.010-in. and the longitudinal cracks several inches long developed all around the circumference at several points along the length of the tube. On subsequent passes the cracks lengthened and ran nearly the full length of the tube by the end of six passes.

6.5 Disassembly Studies - G. A. West

6.5.1 Saw Concept

A design has been made of a remotely operated abrasion disc saw that will make transverse cuts only in removing end boxes and separating core and blanket fuels of spent reactor fuel handles. (Fig. 6.4). A cost estimate will be made of this conceptual design and it will be compared to the cost of a saw that is capable of making both transverse and longitudinal cuts.

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Fig. 6.4

6.5.2 Electrical Discharge Cutting

Tests on the Elox electrical discharge machine are continuing, to evaluate its use in disassembling spent reactor fuel elements. (See UNOP Monthly Report November 1956, CF#-56-11-143). A system of cutting longitudinally with a 0.0201-in. dia brass wire has been demonstrated (Figs. 6.5 and 6.6) and a coolant tank to accomodate elements up to 6 ft in length has been fabricated and is ready for installation.

A cutting rate of 0.021 in.³/hr was the maximum obtained for longitudinal cutting of type 347 stainless steel, 1/16-in. x 24-1/2 in. The catalog cutting rate for this machine is 0.036-in.³/min.

The Elox machine was adopted for wire electrode cutting by mounting pulleys and motor driven reels for continuous reeling of the wire. The attachment is on the vertical feed head and is automatically fed by a servo motor which maintains the desired gap (~0.002-in.) between the electrode and material. Cutting occurs simultaneously across the entire length of the material as the wire is moved at a set rate. The speeds investigated ranged from 67 to 120 ft/hr. It was found that cutting was as efficient with the wire reeled at a low speed as at a high speed. From the appearance of the used wire, a more efficient consumption of the electrode could be realized at still a slower speed of about 40 ft/hr. This speed is to be tried in future tests. Tests are also to be made to determine the use of water as the coolant instead of oil.

From the demonstration runs made on the Elox machine, the present conclusions are: (1) that its cutting rate is too slow for continuous production plant use, but (2) it may be valuable in a few cases of difficult disassembling of fuel elements.

6.6 Discharging Dissolver Solids

C. V. Chester

The development of power reactor fuels with nitric-insoluble clads on nitric-soluble cores make desirable a dissolver with some form of solids discharge. In such a device the soluble core could be leached out of sheared sections of the element with nitric acid, and the solution treated by a conventional solvent extraction plant. The need for more exotic dissolution reagents would be obviated in this case.

A continuous, solids-discharging dissolver has been designed. Figure 6.7 is a drawing of the dissolver showing most of the features. Demonstration runs using sheared pieces of stainless steel clad natural U rods will be made.

Continuous solids discharge is achieved by means of a flat, cylindrical bucket assembly, rotating in the vertical plane, in a stationary tank half full of acid. The buckets are fed from and discharge to the hub. The first model is designed to be critically safe. The bucket assembly is supported

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42 Fig-6.5

Fig. 6.5

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Fig. 6.6

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Figure 6.7 Critically Safe Rotary Slab Dissolver with Continuous Solids Feed and Discharge.

on rollers around its periphery. A central shaft is provided for speed regulation. The assembly will be self-driving due to the difference in weight between freshly charged slug sections on one side and leached out clad on the other. Final drawings have been prepared for an experimental model 2 ft in dia. Estimated cost of the experimental model is \$3740.

6.7 Pulse Column Interfacial Crud Removal

R. J. McNamee, F. L. Rogers, J. R. Eblen

To avoid the extraction and/or entrainment of activity from interfacial crud into the organic product, it would be desirable to remove this crud from the interface in the settling section at the top of an extraction column. A method of effecting this by continuously removing liquid from the column interface, filtering it, and returning the filtrate back to the interface was developed (see UNOP November Monthly Report CF#-56-11-143), using a Fulflo (glasswool) filter and a Lapp pump.

This system was installed on the 2-in. dia 26 ft tall pulse column in Building 3503, and "cold" Thorex A column runs were made. Initial results were most encouraging.

The column was run long enough without using the interface recirculation loop to build up an appreciable amount of crud. When the recirculation system was turned on at a rate of 300 cc/min, this initial crud (up to 4 in.) in the 4-in. dia settling section was removed in less than 1 hr, leaving a clean interface, which could be maintained during the remainder of the run, as long as the recirculation system continued in operation. This was demonstrated repeatedly. The coarse mesh Fulflo seemed to work as well as the fine mesh.

On the last several runs, using the same conditions, severe emulsions at the interface were encountered. The recirculation system did not remove this emulsion; but worsened the condition. The reason for this inconsistent behavior remains unexplained.

6.8 Materials Evaluation - Corrosion Studies

G. A. West, G. B. Dinsmore

The corrosion studies of materials of construction for the Darex and Zircex process of the power reactor fuel reprocessing were discontinued. The tests on titanium were discontinued after 500 hr in boiling solutions of 2N, 8N, and 15.7 N $\text{HNO}_3\text{-UCl}_3$ (11 g/liter). The corrosion rates were negligible (<0.5 mpy) for all concentrations. Titanium is satisfactory for use as a material of construction where only the $\text{HNO}_3\text{-UCl}_3$ solutions are employed in the uranium recovery process. It is not recommended for the combined hydrochlorination step in Zr-U at $\sim 500^\circ\text{C}$ followed by the dissolution of UCl_3 in nitric acid. Future material evaluations will be made by the Battelle Memorial

Institute under a subcontract for corrosion studies for the Power Reactor Fuel Reprocessing program.

6.9 Radiation Damage Studies - G. A. West

6.9.1 Paints

Rescheduling of the operation of the HRT facility has delayed this study for an indefinite period.

6.9.2 Materials Testing

An access tube has been installed in the LITR source which will accomodate various materials for radiation testing. Specimens of Haveg 093 have been ordered for radiation testing. This material is resistant to HF and is to be tested in a high radiation field to evaluate its use as a vessel in which the zirconium-uranium alloy fuels may be dissolved with aqueous HF.

7.0 SUBCONTRACT PROGRESS REPORTS

Thermal Diffusion in Aqueous Salt Solutions - Initial Report of Activities Carried Out Under Subcontract No. 1056, Department of Chemical Engineering, University of Tennessee

R. M. Boarts - Project Director

J. W. Prados - Principal Investigator

As set forth in the above named subcontract, the over-all purpose of the investigation is the development and performance analysis of a process for the separation of metallic elements by thermal diffusion. At present, efforts are being directed towards separation of aqueous solutions of the metallic salts. It is hoped that the relatively high mobility of metallic ions, plus the ease of preparing and handling aqueous solutions may make this an attractive process.

It is planned to carry out the separation in a horizontal thermal diffusion column of the type conceived by S. H. Jury and described in the recent literature.¹ The horizontal column offers several distinct advantages including positive control over process flow rates and elimination of the undesirable "forgotten effect" observed in the conventional Clusius-Dickel column. However, eventually some runs on a Clusius-Dickel unit are contemplated in the hope of obtaining some direct comparison of the performance of the two systems.

To obtain a basis for rational design of a horizontal thermal diffusion column it is necessary to develop a theory of operation for the unit, thereby enabling one to predict the separation factors and heights of transfer units to be expected. Physical data on the systems to be separated are also required, and in particular, one must know the thermal diffusion coefficient and molecular diffusion coefficient for each of the components in the mixtures to be separated.

The development of the column theory is presently being undertaken. Since a rigorous theory leads to non-linear differential equations, several cases are being considered under various simplifying assumptions. It is hoped that one or more of these may be used to approximate with reasonable accuracy the behavior of an actual column.

Thermal and molecular diffusion coefficient data are available for a large number of aqueous salt solutions but at present such data are non-existent for multi-salt systems. Hence units are being constructed for the determination of these coefficients. A method has been proposed² for predicting thermal diffusion coefficients for two-salt solutions when those for the single salts are known. This method will be tested using the data obtained from the units being built.

7.1 Theoretical Investigations Undertaken

To analyze the performance of a horizontal thermal diffusion column, it is necessary to solve simultaneously the equations of hydrodynamics, transport,

1 Chemical Week, July 7, 1956, pp. 52-59.

2 Guthrie, G., et. al., J. Chem. Phys., 17, 310-13 (1949).

and continuity in the three regions consisting of the upper and lower channels and the separating membrane of the column. As previously mentioned, inherent non-linearities in these equations necessitate simplifying assumptions in order to obtain a usable solution. Two cases involving the separation of a two-component system have been treated by Von Halle³, and a third case has been developed under the present contract. Extension of one or more of these cases to a three-component separation (as would be the situation involving two metallic salts and water) will be the next theoretical undertaking. It is also planned to investigate the transient behavior of the column in order to obtain a prediction of the time for attainment of steady state.

7.2 Experimental Equipment Constructed

The thermal diffusion coefficient for a system is most easily obtained by measuring the Soret coefficient which is the ratio of the thermal diffusion coefficient to the molecular diffusion coefficient. Independent measurement of the molecular coefficient is also required.

The Soret coefficient can be obtained from a batch, or "single stage", apparatus in which the solution to be studied is subjected to a temperature gradient in a closed cell. After steady state has been attained the Soret coefficient can be calculated from the measured concentration and temperature gradients in the system. Two such pieces of apparatus differing in mechanical design have recently been constructed. They will be placed in operation as soon as two constant temperature baths, now on order, are received. A simple batch system is presently available for the measurement of molecular diffusion coefficients, and it is hoped to begin measurements of both the Soret and molecular diffusion coefficients about January 1, 1957.

7.3 Major Items of Equipment Purchased

Three major items of equipment have been purchased for the investigation; the two constant temperature baths mentioned previously, and a multiple-point temperature recording potentiometer for measurement of the temperature gradients in the Soret cells, and later in the column. These items were selected on the basis of quotations obtained from at least three reputable bid was accepted in all cases. Delivery on the constant temperature baths was promised for the second week of December 1956. Delivery of the temperature recorder cannot be obtained before March 1957. However, it is planned to use a manually operated potentiometer to read thermocouple outputs until the recorder arrives, in order not to delay the start of the experimental work.

³ Von Halle, E., unpublished research on Thermal Diffusion in Organic Liquids, to appear as part of a Doctoral Dissertation, University of Tennessee, 1957.

7.4 Projected Activities

The major experimental work for the coming three months will involve the measurement of the Soret coefficients for some more common aqueous two-salt solutions, e.g., $\text{NH}_4\text{Cl}-\text{NaCl}$; $\text{Na}_2\text{CO}_3-\text{K}_2\text{CO}_3$; $\text{Ca}(\text{NO}_3)_2-\text{Zr}(\text{NO}_3)_2$; $\text{MgCl}_2-\text{ZnCl}_2$. It is presumed that the Union Carbide Nuclear Company will have certain systems of interest to them, which will also be studied.

The detailed design of a horizontal thermal diffusion column will be undertaken in the near future. It is hoped that detailed drawings can be submitted to the shop for construction by February 15, 1957, and that the column can be placed in operation during the month of April, 1957. Heights of transfer units and separation factors obtained from this column can be used to test the validity of the various theories developed.

7.5 Project Personnel

R. M. Boarts, Project Director
J. W. Prados, Principal Investigator
G. T. Fisher, Research Assistant
S. H. Park, Graduate Assistant (No compensation, M. S. Thesis)
M. B. Hale, Undergraduate Student (No compensation, B. S. Thesis)

7.6 References

1. Chemical Week, July 7, 1956, pp. 52-59.
2. Guthrie, G., et.al., *J. Chem. Phys.*, 17, 310-13 (1949).
3. Von Halle, E., unpublished research on Thermal Diffusion in Organic Liquids, to appear as part of a Doctoral Dissertation, University of Tennessee, 1957.

8.0 VOLATILITY

J. T. Long

8.1 HF Dissolution - C. L. Whitmarsh

HF dissolution is a process designed to dissolve heterogeneous fuel elements, such as those in the STR, by hydrofluorination in a fused salt system. A small scale dissolver study will be carried out by the Unit Operations Section. The process equipment was designed and is now being fabricated in the shop. The equipment installation diagram has also been submitted. Plans for a cubicle, enclosing the area in front of cells 4A and 4B on the second floor of Building 4505, have been accepted and construction is scheduled for early 1957.

8.2 Fluorine Disposal - S. H. Stainker

Fifty-three shakedown and scoping runs, a preliminary examination of tower corrosion, several minor column modifications, and 27 experimental runs were completed in the pilot plant spray tower during the period August 23 to October 16, 1956.

The purpose of these tests was to determine experimentally the effects of the several process variables on the scrubbing efficiency of a multiple spray fluorine disposal tower. These data should provide sound design bases for future disposal towers. The present scope of the investigation is:

- (a) fluorine rates: 0.4 to 2.74 scfm
- (b) potassium hydroxide rates: 3 to 21 gpm
- (c) potassium hydroxide concentrations: 1, 1.5, and 2 N
- (d) initial gas concentration: 20 to 100% F₂ (the remainder, nitrogen)

The maximum fluorine rate is currently determined by the use of a 3/8-in. dia. tubing gas feed line. The period August 23 to October 4, 1956, was spent in defining efficient operating procedures, training operating personnel, and locating and correcting instrumental and mechanical malfunctions. Fifty-three runs were made to minimize operational difficulties and to outline the parameters of the column operation (Table 8.1). Since a topical report will be issued at the conclusion of this experimental program this report will be limited to general comments.

TABLE 8.1

Summary of Preliminary Runs

Volatility Pilot Plant Fluorine Disposal System

Runs made August 23 to October 4, 1956

- Conditions: (1) Gas flow rates are given under run conditions, and have not been corrected to STP, or for purity of fluorine.
- (2) Runs 1 through 11, all nozzles were Schutte and Koerting Fig. 622A, 60 degree fine spray nozzles.
- (3) Runs 12 through 53, top three nozzles were Schutte and Koerting Fig. 622C, 30 degree coarse spray nozzles, lower four nozzles were Fig. 622A.
- (4) These runs were conducted primarily to obtain operating experience, to check analytical methods, and to outline problem areas.
- (5) Runs 1 through 53, were made recirculating KOH from the surge tank to the tower, then back to the surge tank.
- (6) Blank spaces in table indicate that those data were not available.

Run No.	Fluorine Flow Rate (cfm)	Nitrogen Flow Rate (cfm)	KOH Flow (gpm)	No. of Spray Nozzles	Type of Spray	KOH Concentration Initial Normality	KOH Conc. Final Normality	KOH Bulk Temp.-Initial (°C)	KOH Bulk Temp.-Final (°C)	Fluorine Conc. in Off-gas (ppm)	Tower Temp. Max.-External Wall (°C)	Comments
1	0.8	3	10-1/2	7	fine		-	-	-	-	-	Fluorine odor noted around surge tank.
2	1.5	1.5	10-1/2	7	fine	1.68	0.61	-	-	-	-	Stable operation 1030 to 1330. No odor detected.
3	1.5	1	10-1/2	7	fine	2.26	1.95	-	-	38	-	90 minute stable operation.
4	≤ .8 ^(a)	0	-	-	-	-	-	-	-	varied	-	Testing fluorine detector.
5	≤ .8	0	-	-	-	-	-	-	34-1/2	varied	-	Testing fluorine detector.
6	1.4	0	10-1/2	7	fine	1.56	1.29	33	40	-	74	Studying heat generation. 36-minute run.
7	1.8	0	10-1/2	7	fine	1.42	1.19	41	48	-	110	Studying heat generation. 24-minute run.
8	2.4	0	11-1/2	7	fine	1.26	0.82	35	59	-	87	Increased flow through 2 top sprays. Lowered max. temp.-evened out temp. distribution. Material balances at this point varied 10 to 15%. 60 minute run.
9	1.5	0	10-1/2	7	fine	-	-	-	-	-	200	-
10	0.9	0	14	7	fine	-	-	-	-	0	~100	Flow increased to two top sprays.
11	1.3	0	12-1/2	7	fine	-	-	-	-	0	120	Installed 3 coarse spray nozzles in top 3 positions before Run 12.
12	1	1	11-1/2	7	3-coarse 4-fine	-	-	-	-	~100	46	-

TABLE 8.1 (Continued)
Summary of Preliminary Runs

Run	Fluorine Flow Rate (cfm)	Nitrogen Flow Rate (cfm)	KOH Flow (gpm)	No. of Spray Nozzles	Type of Spray	KOH Concentration Initial Normality	KOH Conc. Final Normality	KOH Bulk Temp.-Initial (°C)	KOH Bulk Temp.-Final (°C)	Fluorine Conc. in Off-gas (ppm)	Tower Temp. Max.-External Wall (°C)	Comments
13	.6	.5	.96	1	coarse	-	-	-	-	800	-	Fluorine detector responds more noticeably to sampling rate than to changes in major column conditions.
14	.6	.5	.92	1	coarse	-	-	-	-	to 3800	-	same
15	.4	0	1	1	coarse	-	-	-	-	7622	-	
16	.3	0	1.1	1	coarse	-	-	-	-	9100	-	
17	.5	.4	1.8	1	coarse	2.2	-	-	-	1600	-	
18	.5	.5	2.6	1	coarse	2.2	-	-	-	2100	-	
19	.3	0	1	1	coarse	-	-	-	-	2200	-	
20	.3	0	1.5	1	coarse	-	-	-	-	5600	-	Note effect of liquid rate.
21	.3	0	2	1	coarse	-	-	-	-	5300	-	
22	.4	0	2.5	1	coarse	-	-	-	-	0	-	
23	.4	0	2	1	coarse	-	-	-	-	0	-	
24	.4	0	2	1	coarse	1.92	-	-	-	11000	-	Note discrepancy in Run 24.
25	.4	0	2-1/2	1	coarse	-	-	-	-	0	1	
26	.4	0	2-1/3	1	coarse	-	-	-	-	0	-	Note results Runs 22 through 28.
27	.4	0	2	1	coarse	-	-	-	-	0	-	
28	.4	0	2.2	1	coarse	1.74	1.43	-	-	125	-	40 minute run.
29	.6	0	2.4	1	coarse	-	-	-	-	50	-	
30	.6	0	2.8	1	coarse	-	-	-	-	0	-	
31	.8	0	2.8	1	coarse	.90	-	-	-	high	-	KOH flow immediately increased.
32	.8	0	3.3	1	coarse	.67	-	-	-	41	-	
33	.8	0	3.1	1	coarse	.62	-	-	-	52	-	
34	.24	0	2.1	1	coarse	2.16	-	-	-	high	-	
35	.24	0	2.3	1	coarse	-	-	-	-	342	-	
36	.41	0	3.3	1	coarse	1.61	1.51	-	-	40	48	
37	.41	0	3.0	1	coarse	-	-	-	-	64	59	
38	.41	0	2.75	1	coarse	-	-	-	52	56	59	
39	.41	0	2.5	1	coarse	-	-	-	52	63	60	
40	.41	0	2.25	1	coarse	-	-	-	52	80	61	
41	.41	0	2.0	1	coarse	-	-	-	-	64	-	
42	.41	0	2.1	(a) 1	coarse	-	-	-	-	-	124	(a) 3rd from top nozzle.

TABLE 8.1 (Continued)

Summary of Preliminary Runs

Run	Fluorine Flow Rate (cfm)	Nitrogen Flow Rate (cfm)	KOH Flow (gpm)	No. of Spray Nozzles	Type of Spray	KOH Concentration Initial Normality	KOH Conc. Final Normality	KOH Bulk Temp. Initial (°C)	KOH Bulk Temp. Final (°C)	Fluorine Conc. in Off-gas (ppm)	Tower Temp. Max.-External Wall (°C)	Comments
43	.41	0	2.0	(b) 1	coarse	-	-	-	52	54	70	(b) Top nozzle in operation again.
44	.41	.5	1.75	1	coarse	1.1	-	-	52	0	64	
45	.44	0	2.0	(c) 1	fine	-	-	39	39	10500	40	(c) 7th from top nozzle.
46	.44	0	2.0	(d) 1	fine	.95	-	39-1/2	39-1/2	8900	41	(d) 6th from top nozzle.
47	.44	0	2.0	(e) 1	fine	-	-	40	42	6100	44.5	(e) 5th from top nozzle.
48	.44	0	2.0	(f) 1	fine	.84	-	-	44	5500	45	(f) 4th from top nozzle.
49	.44	0	2.0	(g) 1	coarse	-	.82	-	43	6000	46	(g) 3rd from top nozzle.
50	.4	0	20	7	3 coarse 4 fine	-	-	-	-	0	-	
51	.4	0	3	1	coarse	-	-	-	-	31	-	
52	.4	0	4.9	(h) 2	coarse and fine	-	.60	-	-	16	-	(h) 4th from top nozzle cut in capacity test.
53	2.8	0	20	7	3 coarse 4 fine	2.2	-	-	-	0	-	

The shakedown runs showed the main design fault to be lack of provision for a cooling system to remove the heat of the F_2 -KOH reaction. External tower wall temperatures greater than $100^\circ C$ were recorded during a few runs using Schutte and Koerting Fig. 622A, 60 degree fine spray nozzles. Replacement with coarser spray nozzles (S and K Fig. 622C, 30 degree) permitted 2.7 cfm of fluorine to be contacted at tower wall temperatures less than $80^\circ C$. The decrease in temperature is believed to be caused by decreased interfacial area and increased liquid flow rate.

The tower was opened after approximately 800 ft^3 of fluorine had been contacted at temperatures up to $110^\circ C$. Examination of the monel fluorine inlet pipe revealed severe attack on the inner pipe wall about 1/4-in. from the end inside the tower. This erosion was approximately 1/8-in. deep, 1/8-in. wide, and 1-in. long. The outer surface of the pipe which had been exposed to F_2 , KOH, F_2O , HF, and H_2O appeared to have been copper-plated (or nickel depleted) in patches. A multi-colored scale had formed generally over the surface. The spectrographic analysis of the scale indicated that copper, potassium, and nickel cations constituted the bulk of the material, although calcium ions were present to a limited extent.

The interior tower wall was visually examined through several of the spray nozzle entrance ports. A black scale which was probably nickel hydroxide had coated the top of the column not directly contacted by the sprayed KOH. The lower portions of the column which were swept by the liquid spray appeared to have a clean metallic surface.

Effect of Temperature

Temperature has been proposed as an important factor in the reaction:
 $F_2 + 2 \text{ KOH} \longrightarrow 2 \text{ KF} + \text{H}_2\text{O} + 1/2 \text{ O}_2$. It is believed that an intermediate step ($F_2O + 2 \text{ KOH} \longrightarrow 2 \text{ KF} + \text{H}_2\text{O} + \text{O}_2$) is the rate controlling reaction and is strongly temperature dependent. Some attempts to elucidate this effect are being made in the current runs (Table 8.2).

Summary of Experimental Runs

Volatility Pilot Plant Fluorine Disposal System

Runs from October 5, to October 15, 1956

- Conditions:
- (1) Gas flow rates are the nominal values set for each run and have not been corrected to STP, or for purity of the fluorine, which is about 92%.
 - (2) Fluorine flow during a given run had a maximum fluctuation of about 5%.
 - (3) Liquid flow rates were set by using calibration curves of flow vs. pressure for each nozzle. All liquid flows are multiples of 3 gpm per nozzle.
 - (4) All spray nozzles were Schutte and Koerting Fig. 622C-30° coarse spray nozzles.
 - (5) Off-gas analyses for fluorine are believed to be accurate to within $\pm 10\%$ above a concentration of 100 ppm in these runs.
 - (6) All runs except 206 were made passing KOH through the column to a waste drain. 206 was a re-circulation run.

Run	Fluorine Flow (cfm)	Nitrogen Flow (cfm)	KOH Flow (gpm)	No. of Spray Nozzles	KOH Conc.		KOH Temp.		Fluorine Concentration in Off-Gas (ppm)
					Inlet (normality)	Outlet (normality)	In (°C)	Out (°C)	
101	0.4	0	3	1	2.24	2.20	39	33	5760
111	0.4	0	3	1	2.19	2.10	25	28	6860
121	0.4	0	3	1	1.84	1.74	34	36	6348
102	0.4	0	6	2	2.38	2.19	27	30	5350
112	0.4	0	6	2	1.84	1.79	34	34	4723
103	0.76	0	3	1	2.38	2.36	-	-	0
113	0.76	0	3	1	2.25	2.00	22	32-1/2	2680
104	0.76	0	6	2	~2	~2	29	32	<100
105	0.4	0	3	1	1.00	.90	27	32	8710
106	0.4	0	6	2	1.00	1.00	27	30	6280
107	0.76	0	3	1	1.10	1.03	23	33	18650
108	0.76	0	6	2	1.11	1.07	26	27	14300
206	0.4	0	6	2	1.11	.99	-	48	<10
301	1.44	0	3	1	2.14	1.85	31	42-1/2	<100
311	1.44	0	3	1	2.08	1.75	31	44	97
302	1.44	0	6	2	2.09	1.91	31	36-1/2	<100
303	2.74	0	3	1	2.14	1.94	30.5	53	<100
313	2.74	0	3	1	2.04	1.41	30	60	170
304	2.74	0	6	2	2.04	1.68	30	(a)	70
306	1.0	0	6	2	1.09	.88	31	(a)	27000
307	2.74	0	3	1	1.09	.55	28	(a)	77000 (b)
501	1.0	0	3	1	2.09	1.85	28	38	45

56

TABLE 8.2 (Continued)

Summary of Experimental Runs

Run	Fluorine Flow cfm	Nitrogen Flow cfm	KOH Flow gpm	No. of Spray Nozzles	KOH		KOH		Fluorine Concentration in Off-gas, ppm
					Inlet normality	Outlet Conc.	In °C	Out °C	
503	0.72	0.72	6	2	2.39	2.32	30	33	4960
504	1.37	1.37	6	2	2.39	2.27	30	36	9200
505	0.4	1.6	6	2	2.21	2.14	27	28.2	1390
507	0.29	1.15	6	2	2.11	2.07	27.5	28.5	1220
509	0.55	2.19	6	2	2.09	1.88	28	32	30

(a) out of order

(b) column pressurized

8.3 Gas-Liquid Contacting Studies in 12-in. Tank

C. L. Whitmarsh, J. L. Whitten

Design data for dip tube and draft tube gas-liquid contactors were obtained with a CO_2 -NaOH system. The experimental conditions are an attempt to simulate the fluorine-fused salt conditions in the Volatility Pilot Plant. The variables studied to date were gas flow rate (0.25-6.0 cfm), draft tube diameter (1/2-3 3/4 in.), draft tube gas inlet diameter (10-25 mm), dip tube diameter (5-50 mm), height of dip tube outlet above tank bottom (1/2-4 in.), radial position of horizontal outlet dip tubes ($0.1 = R/R_o$), NaOH concentration (1/90 to 2/9 N), and CO_2 partial pressure (50-100%). The efficiency of utilization of CO_2 was used to correlate all the above variables.

Design data for the fluorinator in the Volatility Pilot Plant is being obtained with a CO_2 aq. NaOH gas-liquid system instead of a fluorine-fused salt system, because of the experimental difficulties associated with fluorine reactivity and high temperature equipment. Preliminary considerations of the type of contactor needed ruled out any mechanical agitator or recirculation device for pilot plant use.

The process conditions - 600-700°C, very corrosive system, and high radioactivity - pointed out the need for a simple, easily fabricated gas-liquid contactor. The dip tube and draft tube (air-lift pump) are being used in the present tests.

Experimental test conditions were established to simulate pilot plant conditions. A Lucite tank, 12-in. i.d. x 38-in. high, was used as the liquid container through which gas was forced under pressure of 20 psig at rates from 0.5 to 6.0 scfm.

Data correlation was shown by plotting the efficiency of utilization of CO_2 versus the various design variables that have been studied. This efficiency is defined as the stoichiometric amount of CO_2 required to react with the NaOH in the solution divided by the actual amount introduced into the solution. At a constant flow rate this reduces to the ratio of the theoretical reaction time to the actual reaction time.

Gas utilization efficiency decreased with increasing gas flow rate (see Table 8.3). At a gas rate of 0.25 cfm the baffled draft tube was most efficient (56%) and the dip tube least efficient (35%) while the unbaffled draft tube was intermediate in its effect (efficiency 44%).

TABLE 8.3

Effect of Gas Flow Rate on the Efficiency of Utilization of CO₂

Conditions: Gas - CO₂ measured at 20°C and 1 atm

Solution - 45 liters of 1/45 N NaOH, depth = 24.3 in.

Tank - 12 in. i.d.

Description of Contactor	Gas Flow Rate ccfm	Average Reaction Time sec	Theoretical Reaction Time sec	Efficiency %
Draft Tube	0.25	469.0	204.0	43.5
1 15/16 in. i.d.	0.5	334.0	102.0	30.5
20 in. length	1.0	141.5	50.9	36.0
10 mm i.d. Horiz. Gas Inlet 1 in. from tube bottom	2.0	90.5	25.4	28.1
Located at center of Tank cross section and 2 in. from tank bottom	3.0	62.8	17.0	27.1
	4.0	49.1	12.7	25.9
	5.0	48.4	10.2	21.1
	6.0	38.2	8.5	22.2
Dip tube	0.25	577.0	204.0	35.3
11 mm i.d.	0.5	315.5	102.0	32.4
Located on the vertical axis of the tank and with the gas outlet 2 in. from the tank bottom.	1.0	157.2	50.9	32.4
	2.0	86.0	25.4	29.5
	3.0	50.1	17.0	33.9
	4.0	41.3	12.7	30.8
	5.0	32.5	10.2	31.4
	6.0	29.0	8.5	29.3

TABLE 8.3 (Continued)

Effect of Gas Flow Rate on the Efficiency of Utilization of CO₂

Conditions: Gas - CO₂ measured at 20°C and 1 atm

Solution - 45 liters of 1/45 N NaOH, depth = 24.3 in.

Tank - 12 in. i.d.

Description of Contactor	Gas Flow Rate cfm	Average Reaction Time sec	Theoretical Reaction Time sec	Efficiency %
Baffled draft tube	0.074	1176.4	689	58.6
Two concentric tubes, 5/8 in. and 4 1/4 in. i.d.	0.22	415.7	232	55.8
The large, outer tube was 18 3/4 in. long and located on the vertical axis of the tank and 1 in. from the tank bottom.	0.50	260.9	102	39.1
Circular donut baffles 3 1/2 in. i.d. and 4 1/4 in. o.d., were spaced every 3/4 in. apart along the length of the large tube.	2.0	146.6	25.4	17.3
	5.0	96.3	10.2	10.6
Same as above except alternate baffles were smaller donuts, 3/4 in. i.d. and 1 1/4 in. o.d., and were attached to the small concentric tube.	0.50	324.7	102	31.4
	2.0	165.1	25.4	15.4
	5.0	100.7	10.2	10.1

At a gas rate of 5.0 cfm the relative efficiencies were reversed with the dip tube, plain draft tube, and baffled draft tubes showing efficiencies of 31, 21, and 11% respectively. At low gas rates the diameter of the draft tube had little effect on efficiency but at high gas rates the efficiency dropped rapidly with decreasing diameter (Fig. 8.1 and Table 8.4). No effect on efficiency was produced when the gas inlet to a 1-15/16 in. dia draft tube was changed from 9.5 mm to 25 mm at gas rates from 0.5 cfm to 5.0 cfm (Fig. 8.2 and Table 8.5).

Anomalous results were obtained when the diameter of the dip tube was varied (Fig. 8.3 and Table 8.6). No explanation can be offered for the minimum efficiency with a 25 mm dia dip tube. Another anomaly appeared in studying the effect of depth of dip tube immersion on gas utilization efficiency, in that lower efficiencies were obtained at a gas rate of 2.0 cfm than at 5.0 cfm (Fig. 8.4 and Table 8.7, contra. Table 8.3). It was shown that efficiency increased with increasing dip tube immersion (and therefore longer contacting time) until the dip tube was less than an inch from the bottom of the vessel. The optimum location for the dip tube within a 12-in. dia right circular cylinder was midway between the center and the circumference except at high gas rates (Fig. 8.5 and Table 8.8). Lowest efficiencies were obtained with the dip tube at the vessel wall.

The reaction driving force was changed by increasing the initial NaOH concentration and by diluting the CO₂ with air. Increasing the NaOH concentration from 0.5 N to 10 N caused an increase in gas utilization efficiency from 23 to 34% (Fig. 8.6 and Table 8.9), while decreasing the partial pressure of CO₂ from 100 to 50% resulted in a drop in efficiency from 30 to 26%, (Fig. 8.7, Table 8.10).

Experimental studies in the 12-in. dia tank are summarized in Table 8.11.

8.4 Gas Liquid Contacting Studies in 6-in. Tank

C. L. Whitmarsh, J. L. Whitten

Some tests were made in a 6-in. dia vessel, using the same amount and concentration of NaOH solution as was used in the 12-in. dia vessel. Gas was introduced through a dip tube on a sieve plate. Because of the greater depth of liquid, the contacting time was increased fourfold but the gas utilization efficiency was increased only 60% at 5.0 cfm and 132% at 0.5 cfm (Table 8.12, cf. Table 8.3). It was found that for the range of flow rates from 0.25 cfm to 5.0 cfm the efficiency of a dip tube in the 6-in. dia vessel could be represented by

$$E = 66.5 - 24.1 \log_{10} R$$

where

E = CO₂ utilization efficiency, %

R = CO₂ flow rate, cfm at 20°C and 1 atm

Figure 8.1 EFFECT OF DRAFT TUBE DIAMETER ON
EFFICIENCY OF UTILIZATION OF CO₂

TABLE 8.4

Effect of Draft Tube Diameter on the Efficiency of Utilization of CO₂

Conditions: Gas - CO₂ measured at 20°C and 1 atm

Solution - 45 liter of 1/45 N NaOH, depth = 24.3 in.

Tank - 12 in. i.d.

Draft tube - 20 in. length

Gas inlet - 10 mm i.d., horizontal, and 1 in. from bottom of tube.

Location - The center of the tank cross section and 2 in. from the bottom.

Draft Tube i.d., in.	Gas Flow Rate cfm	Average Reaction Time sec	Theoretical Reaction Time sec	Efficiency %
1/2	0.5	431.3	102.0	23.7
	2.0	293.1	25.4	8.67
	5.0	280.1	10.2	3.64
1	0.5	391.9	102.0	26.0
	2.0	151.2	25.4	16.8
	5.0	116.2	10.2	8.78
1 15/16	0.5	334.0	102.0	30.5
	2.0	90.5	25.4	28.1
	5.0	48.4	10.2	21.1
2 7/8	0.5	361.4	102.0	28.2
	2.0	106.3	25.4	23.9
	5.0	42.3	10.2	24.1
3 3/4	0.5	357.0	102.0	28.6
	2.0	103.3	25.4	24.6
	5.0	42.4	10.2	24.1

Figure 8.2 EFFECT OF GAS INLET DIAMETER OF DRAFT TUBES
ON THE EFFICIENCY OF UTILIZATION OF CO₂

TABLE 8.5

Effect of Gas Inlet Diameter of a Draft Tube on the Efficiency of Utilization
of CO₂

Conditions: Gas - CO₂ measured at 20°C and 1 atm

Solution - 45 liters of 1/45 N NaOH, depth = 24.3 in.

Tank - 12 in. i.d.

Gas Inlet - Horizontal and 1 in. from draft tube bottom

Draft tube - At the center of the tank cross section and
2 in. from tank bottom. (15/16-in. i.d.)

Gas Inlet i.d., mm	Gas Flow Rate cfm	Average Reaction Time sec	Theoretical Reaction Time sec	Efficiency %
9.5	0.5	334.0	102.0	30.5
	2.0	90.5	25.4	28.1
	5.0	48.4	10.2	21.1
13	0.5	340.7	102.0	30.0
	2.0	95.0	25.4	26.7
	5.0	49.3	10.2	20.7
19	0.5	334.5	102.0	30.5
	2.0	90.0	25.4	28.2
	5.0	48.3	10.2	21.1
25	0.5	347.5	102.0	29.4
	2.0	88.3	25.4	28.8
	5.0	45.5	10.2	22.4

Figure 8.3 Effect of Dip Tube Diameter on
Efficiency of Utilization of CO₂

TABLE 8.6

Effect of Dip Tube Diameter on the Efficiency of Utilization of CO₂

Conditions: Gas - CO₂ measured at 20°C and 1 atm

Solution - 45 liter of 1/45 N NaOH, depth = 24.3 in.

Tank - 12-in. i.d.

Dip tube - located at the center of the tank cross section
and 2-in. from the tank bottom

Dip Tube i.d., mm	Gas Flow Rate cfm	Average Reaction Time sec	Theoretical Reaction Time sec	Efficiency %
5	0.5	328.8	102.0	31.0
	2.0	86.6	25.4	29.3
	5.0	34.0	10.2	30.0
10	0.5	315.5	102.0	32.4
	2.0	86.0	25.4	29.5
	5.0	32.5	10.2	31.4
25	0.5	349.8	102.0	29.2
	2.0	88.3	25.4	28.8
	5.0	37.1	10.2	27.5
52	0.5	303.7	102.0	32.9
	2.0	89.1	25.4	28.5
	5.0	35.6	10.2	28.6

Figure 8.4 EFFECT OF HEIGHT OF DIP TUBE OUTLET ABOVE THE TANK
BOTTOM ON THE EFFICIENCY OF UTILIZATION OF CO₂

TABLE 8.7

Effect of the Length of Contacting Path on the Efficiency of Utilization of CO₂

Conditions: Gas - CO₂ measured at 20°C and 1 atm

Solution - 45 liter of 1/45 N NaOH, depth = 24.3 in.

Tank - 12 in. i.d.

Dip tube - 3/8 in. i.d.

Location - at center of tank cross-section

Distance from Tank Bottom in.	Gas Flow Rate cfm	Average Reaction Time sec	Theoretical Reaction Time sec	Efficiency %
1/2	0.5	299.0	102.0	34.1
	2.0	87.7	25.4	29.0
	5.0	32.5	10.2	31.4
1	0.5	301.3	102.0	33.9
	2.0	81.6	25.4	31.1
	5.0	31.1	10.2	32.8
2	0.5	315.5	102.0	32.4
	2.0	86.0	25.4	29.5
	5.0	32.5	10.2	31.4
4	0.5	338.3	102.0	30.2
	2.0	93.3	25.4	27.2
	5.0	35.2	10.2	29.0

Figure 8.5 EFFECT OF RADIAL POSITION OF DIP TUBE
ON EFFICIENCY OF UTILIZATION OF CO_2

TABLE 8.8

Effect of Radial Position of Dip Tube-Outlet on the Efficiency of Utilization of CO₂

Conditions: Gas - CO₂ measured at 20°C and 1 atm

Solution - 45 liter of 1/45 N NaOH, depth = 24.3 in.

Tank - 12 in. i.d.

Dip Tube - 10 mm i.d.

Location - 1 in. from tank bottom

Position of Gas Outlet	Gas Flow Rate cfm	Average Reaction Time sec	Theoretical Reaction Time sec	Efficiency %
Horizontal and at the center of the tank cross section.	0.5	312.9	102.0	32.6
	2.0	91.3	25.4	27.8
	5.0	32.5	10.2	31.4
Horizontal and tangential to a concentric circle having 1/2 diameter of the tank.	0.5	306.7	102.0	33.3
	2.0	85.1	25.4	29.9
	5.0	33.4	10.2	30.6
Horizontal and tangential to the i.d. of the tank.	0.5	376.0	102.0	27.1
	2.0	97.3	25.4	26.1
	5.0	37.0	10.2	27.6
Vertical and at the center of the tank cross section.	0.5	301.3	102.0	33.9
	2.0	81.6	25.4	31.1
	5.0	31.1	10.2	32.8

Figure 8.6 Effect of NaOH Concentration
on the Efficiency of Utilization of CO_2

TABLE 8.9

Effect of Liquid Concentration on Efficiency of Utilization of CO₂

Conditions: Gas - CO₂ measured at 20°C and 1 atm

Solution - 45 liter of aqueous NaOH,
depth = 24.3 in.

Tank - 12 in. i.d.

Contactor - 3/8 in. i.d. dip tube, located along
the central axis of the tank and with
the gas outlet 1 in. from the tank bottom.

Gas Flow Rate - 2.0 cfm

NaOH Concentration moles/45 liter of solution	Average Reaction Time sec	Theoretical Reaction Time sec	Efficiency %
0.5	55.0	12.7	23.1
1.0	96.2	25.4	26.4
5.0	392.3	127	32.4
10.0	749.0	254	33.9

Figure 8.7 Effect of Partial Pressure
 of CO_2 on the Efficiency of Utilization of CO_2

TABLE 8.10

Effect of the Partial Pressure of CO₂ in the Gas Stream on the Efficiency of Utilization
of the CO₂

Conditions: Gas - CO₂ and air measured at 20°C and 1 atm

Solution - 45 liter of 1/45 N NaOH, depth = 24.3 in.

Tank - 12 in. i.d.

Contacting - 3/8 in. i.d. dip tube, located along the central axis of the tank and with the gas outlet 1 in. from the tank bottom.

Total Gas Flow Rate - 5.0 cfm

Gas Flow Rate cfm		Partial Pressure of CO ₂ %	Average Reaction Time sec	Theoretical Reaction Time sec	Efficiency %
CO ₂	Air				
2.5	2.5	50	80.0	20.4	25.5
3.0	2.0	60	65.0	17.0	26.2
4.0	1.0	80	50.4	12.8	25.3
4.5	0.5	90	41.6	11.3	27.2
5.0	0	100	34.3	10.2	29.7
4.0	0	100	44.9	12.8	28.4
4.0	1.0	80	50.4	12.8	25.3
4.0	2.5	61.5	52.4	12.8	24.3

TABLE 8.11

Results from Gas-Liquid Contactor Studies in a 12-in. diameter Tank

Variable	Range	Parameter	Result	Discussion
Gas Flow Rate (bubble size)	0.25-6.0 cfm	Dip Tube	The efficiency varied from 35.3-25.3%. Although the overall effect was decreased efficiency at increased flow rates, there appears to be a minimum in the region of 2.0 cfm. (See Table 8.3).	At high flow rates the increased bubble size at constant frequency (less area of interfacial contact per unit of gas) causes decreased efficiency.
	0.25-6.0 cfm	Draft Tube	The efficiency decreased from 43.5-21.1% with increasing flow rate. (See Table 8.3).	The same effect as in dip tubes except it is more pronounced due to the frictional effects of the draft tube, which becomes significant at high flow rates. This is partly counteracted by the increase in liquid shear. At low flow rates the increase in bubble area per unit of gas becomes the primary factor and results in increased efficiency.
	0.074-5.0 cfm	Baffled Draft Tube	The efficiency decreased from 58.6-10.6% as the flow rate increased. (See Table 8.3)	Shear and frictional forces are even more prominent in this arrangement. Also, the time of contact for a gas bubble is greatly increased due to the longer path.

TABLE 8.11

Results from Gas-Liquid Contactor Studies in a 12-in. diameter Tank

Variable	Range	Parameter	Result	Discussion
Dip Tube Diameter (bubble size)	5-51 mm	Flow Rate		Although the flow rate parameters show a minimum, the relation between diameter and efficiency is obscure. In all cases the ΔE is practically insignificant. This probably indicates that in this range, bubble size is independent of tube diameter.
		0.5 cfm	Efficiency varied from 29.2 to 32.9%.	
		2.0 cfm	Efficiency varied from 28.5 to 29.5%.	
		5.0 cfm	Efficiency varied from 27.5 to 30.0%.	
Draft Tube Diameter (bubble shear)	1/2-3-3/4 in.	Flow Rate		At small diameter the frictional forces resisting flow became the major factor.
		0.5 cfm	Efficiency varied from 23.7 to 30.5%.	
		2.0 cfm	Efficiency varied from 8.7 to 28.1%.	
		5.0 cfm	Efficiency varied from 3.6 to 24.1%.	
			Rapid increase in efficiency as diameter increases to 2 in., and essentially constant thereafter.	

TABLE 8.11
(Continued)

Variable	Range	Parameter	Result	Discussion
Diameter of Gas Inlet to Draft Tube (bubble size)	9.5-25 mm	Flow Rate 0.5 cfm	Efficiency varied from 29.4 to 30.5%.	The results here are analogous to dip tube diameter.
		2.0 cfm	Efficiency varied from 26.7 to 28.8%.	
		5.0 cfm	Efficiency varied from 20.7 to 22.4%.	
Height of Dip Tube Outlet above Tank Bottom (gas residence time)	1/4 in. - 4 in. (path 24 - 20 1/4 in.)	Flow Rate 0.5 cfm	Efficiency varied from 30.2 to 34.1%.	Shorter residence time decreased efficiency although the change was not considered significant in the range studied. The efficiency showed a maximum as a function of height of dip tube at 2 or 3 flow rates, but will require checking since no explanation is available for this phenomenon.
		2.0 cfm	Efficiency varied from 21.1 to 27.2%.	
		5.0 cfm	Efficiency varied from 29.0 to 32.8%.	
Radial Position of Horizontal Dip Tube Outlet (bulk flow of liquid)	Center-edge	Flow Rate 0.5 cfm	The efficiencies showed a minimum as a function of flow rate. The efficiency decreased almost linearly as the length of bubble path decreased.	The effect of gas outlet position on bulk flow was more important at low flow rates. In all cases the efficiency was about the same as that of a vertical dip tube located at the center of the tank, thus showing that
		2.0 cfm	Efficiency varied from 27.1 to 33.3%.	
		5.0 cfm	Efficiency varied from 26.1 to 29.9%.	
		5.0 cfm	Efficiency varied from 27.6 to 31.4%.	

(Continued)

Variable	Range	Parameter	Result	Discussion
NaOH Concentration (solute concentration)	0.5-10 moles in 45 liter of solution.		<p>The efficiency showed a maximum as a function of flow rate. From the center to 1/2 radius the efficiency was essentially constant, with a sharp decrease at the outer edge.</p> <p>Efficiency varied from 23.1 to 33.9%.</p> <p>The efficiency increased with increasing concentration, although the rate of increase of efficiency decreased.</p>	<p>the liquid bulk flow is not seriously affected by the position or direction (of those studied) of gas outlets.</p> <p>The primary effect is the effect of concentration on the reaction rate for $\text{NaOH} + \text{CO}_2 \rightarrow \text{NaHCO}_3$</p>
Partial Pressure of CO_2 in Gas Stream. (Interfacial area, bulk flow, gas concentration).	50-100%	Constant Total Gas Flow= 5.0 cfm	<p>Efficiency varied from 25.3 to 29.7%.</p> <p>The overall effect was increased efficiency at increased partial pressure.</p>	<p>The effect on the reaction rate again seemed to be the primary factor.</p>
	61.5-100%	Constant CO_2 flow= 4.0 cfm	<p>Efficiency varied from 24.3 to 28.4%. The efficiency increased with increased CO_2 partial pressure.</p>	<p>The increased agitation at the higher flow rates was not enough to counteract the effect of lower reaction rate at lower partial pressures.</p>

TABLE 8.12

Effect of Gas Flow Rate on the Gas Utilization Efficiency

Conditions: Gas - CO_2 measured at 20°C and 1 atm

Liquid - 45 liters of $1/45 \text{ N}$ NaOH, depth = 101 in.

Mixing Tank - 6-in. dia x 150-in. height

Contacting - $1/2$ -in. dia dip tube located on the central axis of the tank and from the bottom.

Gas Flow Rate cfm	*Reaction Time sec	Theor. Time sec	Efficiency %
0.25	247.9	203	81.9
0.50	137.9	102	73.9
1.0	79.4	50.8	64.0
2.0	43.4	25.4	58.5
3.0	30.4	16.9	55.6
4.0	24.8	12.7	51.2
5.0	20.5	10.2	49.8

* Average of two or more runs.

Sieve plates were added to the vessel to obtain smaller bubbles, and thus greater interfacial area, but no increase in efficiency was observed, probably due to the counteracting influence of increased resistance to fluid flow (Table 8.13). In all runs the reaction was complete in the lower part of the vessel first; sometimes by as much as 20 seconds, which represents a 15% increase in efficiency at 0.5 cfm flow rate. A method of increasing bulk circulation in the 6-in. vessel is being sought to take advantage of this potential increase in gas utilization.

TABLE 8.13

Effect of Sieve Plates on the Gas Utilization Efficiency

Conditions: Gas - CO_2 measured at 20°C and 1 atm

*Liquid - 48 liter of $1/45 \text{ N NaOH}$, depth= 109 in.

Mixing Tank - 6 in. dia x 150 in. height

Contacting - $1/2$ in. dia dip tube located on the central axis of the tank and from the bottom.

Sieve Plate and Location	Gas Flow Rate, cfm	Reaction Time sec	Efficiency %
5 7/8 in. dia with holes	0.5	142.3	71.7
Plate was located 1 in. above top of conical base.	2.0	46.5	54.6
Same plate as above except the location was 19 in. above top of conical base.	0.5	143.8	70.9
	2.0	45.4	56.0

* The volume was intended to be 45 liters but an error was discovered after the completion of the runs.